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SPOT TEST DETECTION AND SPECTROPHOTOMETRIC CHARACTERIZATION AND DETERMINATION OF CARBAZOLES WITH 3-METHYL-2-BENZOTHAZOLONE HYDRAZONE, p-NITROSO-PHENOL, AND FLUOROMETRIC METHODS. APPLICATION TO AIR POLLUTION

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APPLICATION TO AIR POLLUTION

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SUMMARY

Carbazole has been detected in some airborne particulate samples. Two spectrophotometric methods for the determination of carbazole are introduced. Beer's law was obeyed from 4 to greater than 90 μg of carbazole in the 3-methyl-2-benzothiazolone hydrazone and p-nitrosophenol procedures. Both methods can be used for the estimation of carbazole in the benzene extracts of airborne particulates. Two new spot tests for carbazole are also introduced. With the p-nitrosophenol test 0.4 μg of carbazole can be detected. This test can be applied to air samples. In strongly alkaline solution 0.2 μg of carbazole can be detected through the brilliant blue fluorescence of the anion.

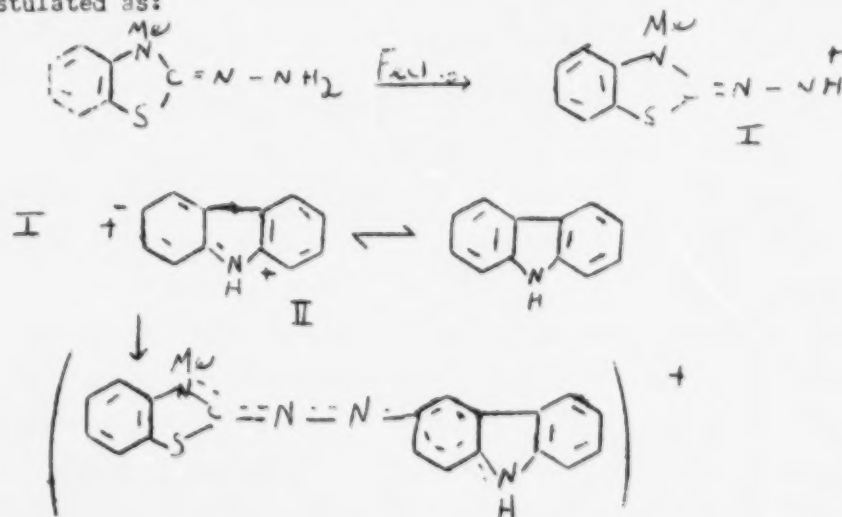
In the column chromatography of the benzene extract of airborne particulates, carbazole, when present, is eluted directly after the coronene fraction. The evidence for the presence of carbazole is based on the ultraviolet absorption spectra in pentane, dimethylformamide and alkaline dimethylformamide solutions, as well as on colorimetric and fluorometric procedures. By the spectrophotofluorometric procedure 0.001 μg of carbazole can be detected in pentane.

Carbazole can be characterized and estimated in the benzene extract of airborne particulates by the nitrosophenol spot test and spectrophotometric procedure, by the 3-methyl-2-benzothiazolone hydrazone spectrophotometric procedure, and by the excitation and emission spectra of the material in pentane, dimethylformamide, and alkaline dimethylformamide.

Application of the 3-methyl-2-benzothiazolone hydrazone spectrophotometric procedure ⁹ to benzene extracts of some airborne particulates and to column chromatographed subfractions of these particulates ⁴ occasionally gave a brilliant blue solution, λ max. 586 m μ .

Consequently it was desirable to ascertain what type of organic compounds would react with the reagent. It has been shown that 3-methyl-2-benzothiazolone hydrazone forms brilliant dyes with aromatic primary amines, their N-alkyl and N,N-dialkyl derivatives, diarylamines, and imino heterocyclic compounds, such as pyrrole, indole, carbazole and phenothiazine.⁹ Formaldehyde reacts with 3-methyl-2-benzothiazolone hydrazone to give a brilliant blue.⁷ Preliminary results which are being further investigated have indicated that azulene derivatives give a brilliant blue with the reagent. Azulene has a high electron density at the 1 and 3 carbon atoms, has a significant dipole moment,² and its ground state structure is postulated as having a strong contribution from zwitterionic forms.¹⁰ Betaine-type structures have also been assigned to the reacting form of azulene.¹ On the other hand, polycyclic hydrocarbons such as pyrene and perylene gave negative results in the test but are much less basic than azulene.

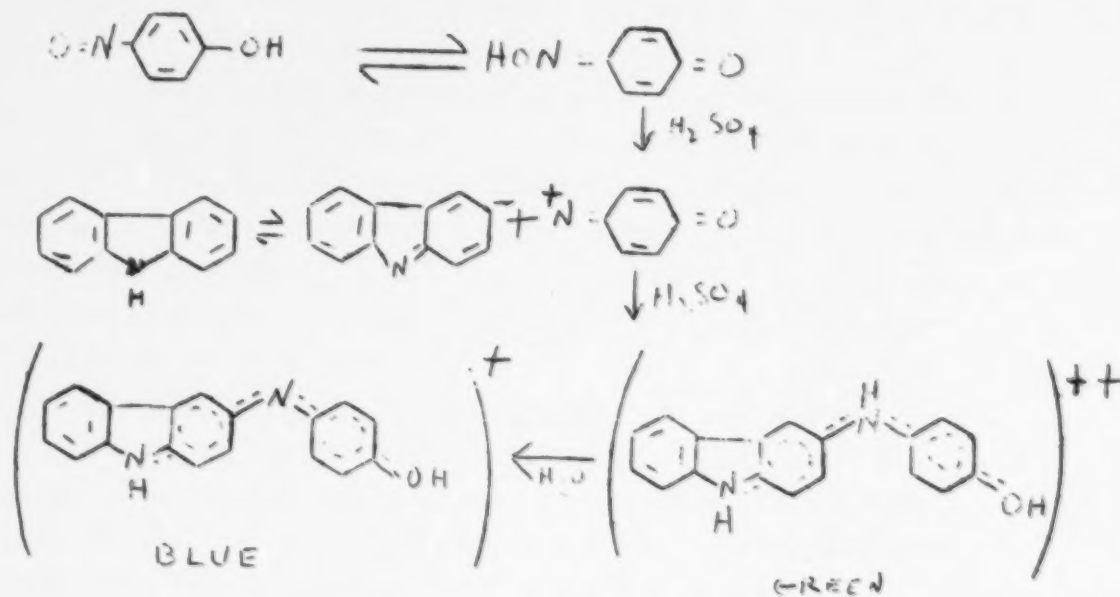
To be attacked by the electrophilic reagent, I, organic compounds must contain a carbon atom, which is a negative resonance terminal in a zwitterionic resonance system, e.g. II, and which consequently has a high electron density. On this basis, the mechanism for the determination of carbazole would be postulated as:



In order to characterize definitely the compound(s) which gave a blue color, λ_{max} 586 m μ , in the 3-methyl-2-benzothiazolone hydrazone procedure, numerous fluorescence and spectrophotometric methods were applied. Only those

of value for carbazole will be described, e.g., the xanthidrol ³ and p-nitrosophenol procedures. The mechanism for the xanthidrol reaction with carbazole derivatives has been described.⁸

The mechanism for the p-nitrosophenol procedures probably consists of the following reactions:



EXPERIMENTAL

Reagents and Equipment. -- 3-Methyl-2-benzothiazolone hydrazone hydrochloride ⁷ was prepared and purified by literature procedures. Xanthidrol and p-nitrosophenol were obtained from Matheson, Coleman and Bell. The p-nitrosophenol was crystallized twice from xylene before use.

A Cary Model 11 recording spectrophotometer with 1-cm cells was used in the absorption spectral studies; the Aminco-Bowman spectrophotofluorometer with 1 cm cells was used for the fluorescence studies; the American Optical Company Rapid Scan Spectrophotometer was used in studying unstable colors.

Reagent Solutions. -- 3-Methyl-2-benzothiazolone hydrazone hydrochloride, 0.4% aqueous solution, stable for at least a week.

p-Nitrosophenol, 0.5% in sulfuric acid, stable for about 4 hours.

Ferric chloride 1% aqueous solution

Acidic methanol, 1 part by volume of concentrated hydrochloric acid diluted with 5 parts by volume of methanol.

p-Nitrosophenol Spot Tests for Carbazole. -- Test I. The test is conducted in the depression of a spot plate. To 1 drop of a 0.5% solution of p-nitrosophenol in sulfuric acid is added 1 drop of methanolic or acetic acid test solution. In the presence of carbazole a green color is obtained, identification limit 0.4 μg . Then 1 drop of water is added. In the presence of carbazole the green color turns blue. In this last step the identification limit is about 2 μg . In both cases the blank is yellow.

Test II. The test is conducted on glass fiber filter paper (No. 934-AH, H. Reeve Angel & Co., Clifton, N. J.). To 2 drops of 0.5% p-nitrosophenol in sulfuric acid is added 1 drop of methanolic test solution. After a 1 minute waiting period the color is read. In the presence of carbazole a bright blue-green color is obtained. The identification limit for carbazole is 0.6 μg . The blank is yellow. N-Methyl- and N-ethyl-carbazole have identification limits of approximately 1 μg .

Fluorescence Spot Test for Carbazole. -- To one drop of a solution of the sample in dimethylformamide on a filter paper is added one drop of 10% aqueous tetraethylammonium hydroxide. The fluorescence color under ultraviolet light is immediately noted, for it gradually fades. A brilliant blue fluorescence with an identification limit of 0.2 μg is obtained with carbazole. 9-Alkylcarbazoles show the same light blue fluorescence in dimethylformamide as in alkaline dimethylformamide, while carbazole has little if any fluorescence in neutral or acidic dimethylformamide solution.

3-Methyl-2-benzothiazolone Hydrazone Spectrophotometric Procedure. -- To 1 ml of the methanolic test solution in a 10 ml volumetric flask is added 1 ml of 0.4% aqueous 3-methyl-2-benzothiazolone hydrazone hydrochloride followed by 2 ml of 1.0% aqueous ferric chloride. The mixture is shaken, allowed to stand for 30 minutes, then diluted to the mark with acidic methanol. The absorbance is determined at the wave length maximum of 586 $\text{m}\mu$ against a blank. The results for several carbazole derivatives are given in Table I.

p-Nitrosophenol Spectrophotometric Procedure. The solid sample containing 10 to 300 μg of a carbazole compound is dissolved by shaking with 1 ml of a concentrated sulfuric acid solution containing 0.5% of p-nitrosophenol. Five minutes after the reagent has been added the mixture is diluted to 10 ml with

concentrated sulfuric acid. The absorbance of the green solution is then read at the wave length maximum within 15 minutes after dilution to the mark. The results obtained for several carbazole derivatives are given in Table I.

RESULTS AND DISCUSSION

Absorption and Fluorescence Spectra of Carbazole. -- Probably the best means of characterization of carbazole (or its derivatives) is by its ultra-violet absorption spectrum in a non-polar solvent such as pentane (Fig. 1). There is much finer structure and the bands are sharper than in a polar solvent such as alcohol or dimethylformamide. However, with a complicated mixture, a satisfactory separation of carbazole must be achieved before such an absorption spectral study is worth attempting. The absorption spectra of carbazole in neutral and alkaline dimethylformamide (Fig. 2) is an additional help in detecting and determining carbazole after separation from a mixture. The alkalization of a dimethylformamide solution of a carbazole compound containing a ring NH grouping causes a strong red shift in the long wave length bands. Formation of the carbazole anion also causes a 3-fold increase in the absorbance of the 290 $m\mu$ band, but the anion is unstable and measurements on the alkaline solution must be made immediately.

These spectrophotometric procedures are much less sensitive and selective for carbazole than spectrophotofluorometric procedures. It is true of many fluorescent compounds that the excitation spectrum obtained at an appropriate emission spectral wave length maximum is much more sensitive and much more selective than the absorption spectrum of the same molecule.⁴⁻⁶

The chief problems in spectrophotofluorometric analysis are the quenching effect of other compounds in the mixture and the greater difficulty in obtaining quantitative data on the spectrophotofluorometer as compared to a spectrophotometer.

A dimethylformamide solution of carbazole shows a striking change in the excitation and emission spectra when the solution is made alkaline with a strong base (Fig. 3). The excitation and emission spectra of carbazole in pentane (Fig. 4) have also been found extremely useful in the characterization and determination of carbazole. The band at 349 $m\mu$ in Fig. 4a is caused by light scattering in the solvent and is a common effect. The excitation

spectrum of carbazole in pentane or dimethylformamide strongly resembles the absorption spectrum in the same solvent. Thus, with a knowledge of organic absorption spectrophotometry the more sensitive and highly selective excitation spectrum could be of value in the identification of an unknown fluorescent compound.

The various procedures cover a wide range of sensitivity. By the xanthidrol method approximately 80 μg of carbazole can be detected spectrophotometrically by the ultraviolet absorption spectrum or the 3-methyl-2-benzothiazolone hydrazone or p-nitrosophenol procedures approximately 4 μg of carbazole can be detected; by the excitation or emission spectrum in a non-basic solvent, 0.001 μg of carbazole can be detected spectrophotofluorometrically.

The range in selectivity of these diverse methods will be discussed in the Applications section.

The p-Nitrosophenol Procedure. -- Variables in the p-nitrosophenol procedure for the determination of carbazole were investigated. Lower concentrations of p-nitrosophenol gave lower intensities (Fig. 5). At concentrations of 0.5 to 2.0% of the reagent a plateau was reached. However, the blank became much more intense with progressively high concentrations of the reagent. Consequently, a concentration of 0.5% of the nitrosophenol in the reagent was chosen as giving the most desirable results.

The color intensity was stable for at least 12 minutes after the solution had been diluted to 10 ml, then it gradually decreased. Beer's law was obeyed from 4 to 100 μg of carbazole.

The nitrosophenol method gave approximately twice the molar absorptivity of the xanthidrol procedure (Fig. 6), but required use of concentrated sulfuric acid.

Polycyclic hydrocarbons such as pyrene, anthracene, and benzo[a]pyrene interfered much less than expected, even though they formed colored solutions in concentrated sulfuric acid. Phenol, anisole, N,N-dimethylaniline, pyrrole, indole, naphthalene, 1-naphthol, 1-methoxynaphthalene, 1-naphthylamine, and azulene gave negative results in the procedure.

The 9-methyl and 9-ethyl derivatives of carbazole did not react as well as carbazole; the 9-acetyl derivative reacted poorly at first but the intensity gradually increased with hydrolysis of the compound to carbazole.

Modification of the procedure for carbazole by dilution with water while cooling, instead of dilution with sulfuric acid, gave a blue solution of the monocation, λ_{max} 615 m μ and ϵ 12000. With this modification the interferences due to polycyclic aromatic hydrocarbons would probably be considerably decreased. However, the color faded fairly quickly - in about 8 minutes the intensity decreased by one half.

These two procedures should be of value in characterizing carbazole derivatives.

The 3-Methyl-2-Benzothiazolone Hydrazone Procedure. The standard procedure was developed from a study of the manifold variables. For a better understanding, the effect of each variable on the standard procedure in the determination of carbazole is summarized here. When the percentage of methanol in the approximately 4 ml of reaction mixture was doubled to about 50%, the intensity decreased to 0.4 of the original value. Though the methanol interfered, the one milliliter used in the standard reaction mixture was necessary to dissolve the carbazole test sample.

A concentration of 0.2% of 3-methyl-2-benzothiazole hydrazone in the reagent gave an absorbance of 1.81. Lower concentrations gave lower values, while concentrations of 0.35 to 2.0% gave absorbance values of 2.00. A concentration of 0.4% reagent was chosen because it gave much lighter yellow blanks than was obtained with more concentrated reagent.

The use of 0.5, 1.0 and 2.0% ferric chloride gave absorbances of 1.41, 2.00 and 2.10, respectively, for a 4.5×10^{-5} M final concentration of carbazole. Lower concentrations of ferric chloride gave lower values; higher concentrations gave greenish colored blanks. The 1% ferric chloride solution gave a somewhat better blank than the 2% solution.

The reaction time study resulted in an absorbance versus time curve which did not reach a plateau even after 1 hr. (Fig. 7). The increase in absorbance is quite steep during the first few minutes but levels off somewhat by 30 minutes, and thereafter there is only a slight increase of 0.04 absorbance units by 60 minutes. For these reasons a 30-minute reaction time was chosen.

After the 30-minute waiting period the addition of 0.2 to 1.5 ml of concentrated hydrochloric acid followed by methanol to 10 ml gave optimum results. With less than 0.2 ml hydrochloric acid the intensity was diminished;

with more than 1.5 ml the test solutions containing carbazole became greener, although the wave length maximum and the intensity remained about the same. Volumes of acid less than 1.0 ml tended to give turbid solutions. With the use of the acidic methanol solution (1 volume of concentrated hydrochloric acid to 5 volumes of methanol) as a diluent, optimum results were obtained.

The color intensity was stable for 2 hours. In 17 hours the absorbance dropped from an initial value of 2.00 to 1.83. Beer's law was obeyed from 4 to greater than 90 μg of carbazole per 10 ml of final solution. Reproducibility was more satisfactory than with the p-nitrosophenol procedure. Absorbance values for the method agreed within $\pm 2\%$. The absorption spectra obtained in the xanthidrol, p-nitrosophenol and 3-methyl-2-benzothiazolone hydrazone determinations of carbazole are compared in Fig. 6.

Anthanthrene, coronene, and benzo[g,h,i]perylene, hydrocarbons which could be present in a poorly separated carbazole chromatographic fraction, gave negative results. Benzaldehyde also did not react. However, aliphatic aldehydes, ⁷ aromatic amines, ⁹ and imino heteroaromatic compounds ⁹ will react. For example, indole gave bands at 462 and 510 $\text{m}\mu$ with molar absorptivities of 19000 and 23,000, respectively.

Ordinarily, aliphatic aldehydes and the basic aromatic amines would not be found in an airborne particulate fraction. The type of absorption spectrum obtained with an aliphatic aldehyde is characterized by a doublet at approximately 635 and 670 $\text{m}\mu$ and could not be mistaken for the spectrum obtained with carbazole.

9-Methyl- and 9-ethyl-carbazole also reacted readily with the reagent giving bands absorbing at longer wave lengths than the carbazole chromogen (Table I).

APPLICATION

The evidence for the characterization of carbazole in the approximately half dozen airborne particulate samples in which it was found is summarized here. Column chromatography on alumina of a mixture of known polycyclic hydrocarbons by a standardized procedure ⁴ clearly indicates that carbazole comes through the column directly after coronene. A similar chromatographic procedure was utilized for several benzene-extracted fractions of airborne particulates that gave a blue color, λ max. 586 $\text{m}\mu$, in the 3-methyl-2-benzothiazolone hydrazone procedure. In these air pollution samples the fraction

following coronene had an ultraviolet absorption spectrum practically identical to that of carbazole (Fig. 1). One characteristic of the spectrum of this fraction must be mentioned, and that is the presence of sharp, well-defined, but much less intense bands at 346, 364, and 383 mμ. These bands are too weak to be shown in Fig. 1. However, when the concentration of this fraction in pentane was twenty times greater, the bands appeared. The structure of the compound(s) from which these bands are derived is unknown.

The excitation and emission spectra in pentane of the carbazole fractions and pure carbazole were identical (Fig. 1). The excitation and emission spectra of the carbazole fractions in acidic or alkaline dimethylformamide were also identical to the analogous spectra of carbazole. The compound found in these air pollution samples is, without a doubt, carbazole.

Comparison of the 3-methyl-2-benzothiazolone hydrazone, xanthidrol and p-nitrosophenol procedures for the determination of carbazole in airborne particulates indicates that the p-nitrosophenol is the simplest. The 3-methyl-2-benzothiazolone hydrazone and the p-nitrosophenol procedures are the most sensitive for the determination of carbazole. A test sample would have to contain 20 times as much carbazole for the xanthidrol method ³ to give the same intensity as obtained with the 3-methyl-2-benzothiazolone hydrazone procedure. However, the xanthidrol method should be capable of a further improvement in sensitivity by slight modification. Thus far, no evidence has been found for any other compound present in airborne particulates reacting with the hydrazone reagent, so the method appears to be specific for carbazole in airborne particulates.

A carbazole fraction obtained from an airborne particulate sample was quantitatively analyzed by the various methods (Table 2). The methods averaged around 67 ± 3 μg of carbazole.

The application of these spectral procedures to the analysis of the benzene extracts of appropriate airborne particulates was next investigated. The fluorescence spot test was of no value here. The p-nitrosophenol spot plate test worked very nicely. A bright green color was obtained. The detection limit for carbazole in benzene extracts of airborne particulates was about 1 μg.

The air samples containing carbazole were analyzed by the 3-methyl-2-benzothiazolone hydrazone and the p-nitrosophenol spectrophotometric procedures and gave spectra containing bands at 586 and 695 m μ , respectively. Consequently, duplicate recovery experiments were performed on a carbazole-free benzene extract of airborne particulates to which known amounts of carbazole were added (Table 3). When fairly large amounts of sample (1-2 mg) containing approximately 7-90 μ g of carbazole are to be analyzed, any of the analytical procedures described in this paper can be used. However, in the 3-methyl-2-benzothiazolone procedure a slight turbidity may result, so it is necessary to run an extra blank containing the benzene extract and everything else except the hydrazone reagent. This extra blank corrects for the turbidity and more reasonable results are obtained.

In the fluorescence methods very much lower concentrations of carbazole can be determined, but the quenching effect of the many other compounds in the mixture has to be standardized by running a Beer's law study on carbazole solutions containing a standard weight of a benzene air particulate fraction and analyzing for carbazole in this weight of material (see 5).

The excitation and emission spectra of a benzene fraction of an air particulate sample at the appropriate wave lengths for the analysis for carbazole are compared to the analogous spectra of pure carbazole (Figs. 8 & 9). Occasionally, a closer similarity of the corresponding spectra of the pollutants fraction and of carbazole has been obtained. Obviously, the methods show promise of further development.

The type of air pollution associated with the presence of carbazole will be discussed in a separate publication, as will the atmospheric composition in terms of polycyclic compounds.

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LIST OF FIGURES

- Figure 1. Ultraviolet absorption spectra of carbazole (10^{-4} M) in pentane (____) and 95% ethanol (- - -). Carbazole fraction of an air sample in pentane (.....). The wave length maxima in millimicrons and molar absorptivity values of carbazole in pentane are as follows: 235 ($\sim$ 30400), 246 (20400), 255 (11800), 274s (5800), 291 (10500), 285 (13000), 291 (19900), 307 (2800), 318 (3600), 323s (2600) and 331 (3800).
- Figure 2. Ultraviolet absorption spectra of carbazole (5×10^{-5} M) in neutral dimethylformamide (- - -) and in alkaline dimethylformamide (____). The alkaline dimethylformamide solution consists of 10 ml of a mixture of distilled dimethylformamide and 0.1 ml of 25% aqueous tetraethylammonium hydroxide. The spectrum of such a solution is determined immediately after the addition of alkali.
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- Figure 5. Effect of the percent of p-nitrosophenol in the reagent solution on the absorbance obtained at λ max. 695 m μ in the standard procedure.
- Figure 6. Visible absorption spectra obtained in the determination of carbazole (5×10^{-5} M) with xanthidrol (3) (.....), p-nitrosophenol (- - -) and 3-methyl-2-benzothiazolone hydrazone (____).

Figures cont.

Figure 7. The effect of oxidation time in minutes on the absorbance obtained in the 3-methyl-2-benzothiazolone determination of carbazole (2.5×10^{-5} M).

Figure 8. Excitation spectra at an emission wave length maximum of 360 $m\mu$ with the meter multiplier set at 0.01 in neutral dimethylformamide: carbazole (5×10^{-7} M) (---) and a benzene soluble fraction of airborne particulates (11 $\mu\text{g/ml}$) (_____).

b. Emission spectra at the excitation wave length maximum of 298 $m\mu$ with the meter multiplier set at 0.01 in neutral dimethylformamide: carbazole (---) and a benzene soluble fraction of airborne particulates (11 $\mu\text{g/ml}$) (_____).

Figure 9. Excitation spectra in alkaline dimethylformamide with the meter multiplier set at 0.03: carbazole (10^{-6} M) at an emission wave length maximum of 425 $m\mu$ (_____) and a benzene soluble fraction of airborne particulates at an emission wave length maximum of 450 $m\mu$ (11 $\mu\text{g/ml}$) (---).

b. Emission spectra in alkaline dimethylformamide with the meter multiplier set at 0.03 at an excitation wave length maximum of 292 $m\mu$: carbazole (10^{-6} M) (_____) and a benzene soluble fraction of airborne particulates (11 $\mu\text{g/ml}$) (---).

TABLE I. COLORIMETRIC DETERMINATION OF SOME CARBAZOLE COMPOUNDS

<u>Compound</u>	<u>Hydrazone Test</u>		<u>p-Nitrosophenol Test</u>	
	<u>λ max.</u>	<u>$\epsilon \times 10^{-3}$</u>	<u>λ max.</u>	<u>$\epsilon \times 10^{-3}$</u>
Carbazole	586	44	695	40
9-Methylcarbazole	595	49	695	26
9-Ethylcarbazole	597	49	695	26

TABLE 2. AMOUNT OF CARBAZOLE IN A CARBAZOLE AIR FRACTION

<u>Method</u>	<u>ug Carbazole</u>
3-Methyl-2-benzothiazolone hydrazone	65
p-Nitrosophenol	67
UV spectra in pentane - total absorbance at 291 m μ	71
UV " " " - base line method at 291 m μ	66
Emission spectra in pentane at λ 349 m μ - Exc. λ 292 m μ	67
Excitation spectrum in pentane at λ 292 m μ - Emis. λ 349 m μ	64

TABLE 3. RECOVERY OF CARBAZOLE FROM AIR SAMPLES

<u>µg Carbazole in sample</u>	<u>µg Carbazole Found</u>		<u>Anal. at Em. λ348 Excited at λ 292</u>	<u>Anal. at Exc. λ292 Emission at λ348</u>
	<u>Hydrazone Method</u>	<u>p-Nitrosophenol Method</u>		
0.17	--	--	0.17	0.15
0.33	--	--	0.32	0.28
0.67	--	--	0.65	0.62
17	19	15	---	---
33	34	28	---	---
69	68	55	---	---